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Emission analysis of RE^{3+} (Eu^{3+}, Tb^{3+} & Ho^{3+}) : B_2O_3–BaO-LiF/AlF_3 glasses

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Abstract : We report here the luminescence spectra of certain rare earth ions (Eu^{3+}, Tb^{3+} & Ho^{3+}) doped B_2O_3-BaO-LiF/AiF_3 based on the measurements of emission and decay curves of prominent emission transitions. For both the reference host glasses, FTIR, XRD, DTA-TG profiles have been recorded to understand their structural and thermal properties. Eu^{3+} doped glasses have shown *five* emission transitions of $^5D_0 \rightarrow {}^7F_{01,2,3\ \&\ 4}$ located at 580nm, 593nm, 615nm, 655nm and 704nm respectively with an excitation at λ_{exci} = 392 nm ($^7F_0 \rightarrow {}^5L_6$). Also under an UV source, these europium glasses have displayed a bright *red* emission from their surfaces. Tb^{3+} glasses have exhibited *four* emission bands of $^5D_4 \rightarrow {}^7F_{6,5,4,3}$ at 491nm, 547nm, 588nm and 625nm respectively with an excitation at λ_{exci} = 376 nm ($^7F_6 \rightarrow {}^5G_6$). Intense *green* emission from the glass surfaces has been noticed upon exposure to the UV source. Prominently bluish-green emission has been noticed from the surfaces of the holmium glasses under an UV source and same emission transition ($^5F_4 \rightarrow {}^5I_8$) at 519 nm with an excitation at λ_{exci} = 389 nm ($^5I_8 - {}^5G_4$) has also been obtained from their measured emission spectra. For all the prominent emissions of the rare earth glasses, decay curves have been measured to compute their lifetimes.

Keywords : Re^{3+} glasses, emission properties

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1. Introduction

Over the past several years, a great deal of work has been carried out in the development and characterization of a wide variety of optical glasses for different applications [1-9]. In recent years, a special interest has been focused towards the production of *fluoro-borate* glasses because of their potential applications as luminescent materials [10-12]. It is interesting to mention that these borate glasses having boron-oxygen groups which could

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be dominantly contributing in luminescence phenomenon thus these glasses have been identified as potential optical materials for their use in *optoelectronics.* We have earlier carried out a preliminary study in understanding the emission spectra of two rare earth (Pr^{3+} & Tm^{3+}) ions doped separately in barium borate (B_2O_3-BaO) glasses with a couple of network modifiers (NWMs) namely LiF & AlF_3 [13]. Now, it is aimed to undertake yet another three rare earth ions such as Eu^{3+}, Tb^{3+} and Ho^{3+} ions that are doped individually in the same [13] host glass matrices of B_2O_3–BaO-LiF/A1F_3 to understand their emission performance. Since these ions are known to be prominently visible color luminescent ions (Eu^{3+} for *red*, Tb^{3+} for *green* and Ho^{3+} for *bluish green*) upon their excitation in the UV region, we have undertaken a thorough study of their emission performances.

2. Experimental studies

Glass Preparation :

Two types of reference host glasses (abbreviated as BBLi and BBAl) without dopant rare earth ions were prepared in the following chemical compositions by means of a conventional melt quenching method.

BBLi	$60B_2O_3$ – 10BaO – 30 LiF
BBAl	$60B_2O_3$ – 10BaO – 30 AlF_3

Accordingly, into these two types of host glass matrices, three rare earth ions such as Eu^{3+}, Tb^{3+} & Ho^{3+} were incorporated each of them separately, hence the following six luminescent optical glasses were prepared for the present investigation alongside the above two reference glasses. The following six glasses were labeled appropriately based on the availability of the luminescent rare earth ion and the other host glass chemicals.

Eu^{3+} : BBLi	0.1 Eu^{3+} : 59.9 B_2O_3 – 10BaO – 30 LiF
Eu^{3+} : BBAl	0.1 Eu^{3+} : 59.9B_2O_3 – 10BaO – 30 AlF_3
Tb^{3+} : BBLi	0.1 Tb^{3+} : 59.9 B_2O_3 – 10BaO – 30 LiF
Tb^{3+} : BBAl	0.1 Tb^{3+} : 59.9B_2O_3 – 10BaO – 30 AlF_3
Ho^{3+} : BBLi	0.1 Ho^{3+} : 59.9B_2O_3 – 10 BaO – 30 LiF
Ho^{3+} : BBAl	0.1 Ho^{3+} : 59.9 B_2O_3 – 10 BaO – 30 AlF_3

The raw chemicals used were of analytical grade H_3BO_3, $BaCO_3$, LiF, AlF_3 and the oxides of rare earths studied. Each batch with 10g of raw chemicals was thoroughly mixed and powdered using an agate mortar and pestle. Each of these batch chemicals was melt in a porcelain crucible at 950^{o}C for an hour in a tubular electrical furnace. The chemical melts were quenched in between smooth surfaced brass plates to obtain transparent clear glasses in 2cm diameter having 0.3 cm thickness.

Measurements :

XRD profiles of the reference host glasses were obtained from the Shimadzu – XD 3A diffractometer with a Ni-filter and CuK_α (1.542Å) radiation with an operating voltage of 30 KV and current of 20 mA with a Si detector at the 2θ values at the rate of two degrees per minute. Thermal behaviors of the reference host glasses were carried out on a TG-DTA analysis (Comptec STA409PC) system from the room temperature upto 1000°C at a heating rate of 10°C/min in an N_2 gas atmosphere. FTIR spectra of host glasses were measured on a Nicolet IR-200 Spectrophotometer using the KBr pellet technique in the range of 400-4000 cm^{-1}. Both excitation and emission spectra of these glasses were recorded on a SPEX Fluorolog-2 Fluorimeter (Model-II) attached with a Xe-arc lamp (150W) with the Datamax software in acquiring the spectral data. Emission decay curves were measured with a phosphorimeter attachment to the system with a Xe-flash lamp (50W).

3. Results and discussion

XRD profiles of the reference host glasses are shown in Figure 1 and from this Figure it is clear that those are of amorphous nature. The FTIR spectra (Figure 2) of the host glasses show the structure of vitreous borates to consist of a random network of BO_3 triangles with a certain fraction of boroxol (six membered) rings; but inclusion of the network modifiers, leads to formation of BO_4 tetrahedra in the borate glass network. In the infrared spectral region, the vibrational modes of borate networks show three regions [14-16]. In the first region, 1200-1600 cm^{-1} band is due to an asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units, the band in the second region is located between 800 and 1200 cm^{-1} is due to the B-O bond stretching of tetrahedral BO_4 units and thirdly a band at 700 cm^{-1} is due to the bending of B-O-B linkages in the borate

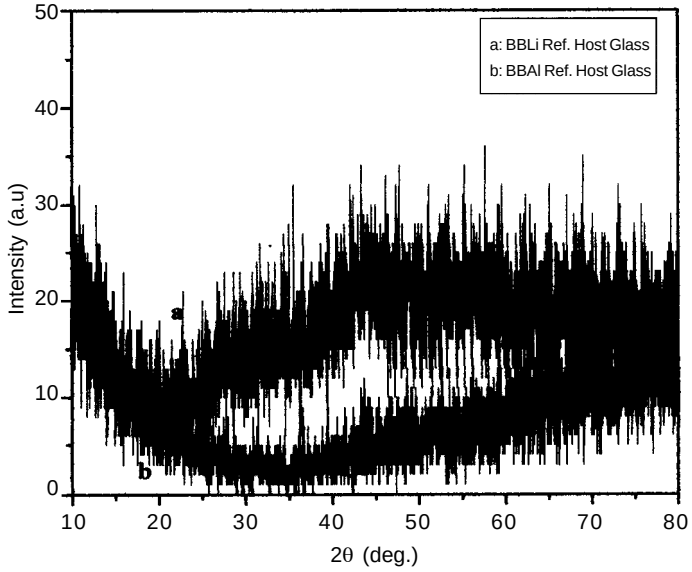

Figure 1. XRD profiles of BBLi and BBAl reference host glasses.

network. Thus, BBLi and BBAl containing host glasses without the dopant rare earth ions have demonstrated the presence of three principle bands located at 1384 cm^{-1}, 994 cm^{-1} and 704 cm^{-1} along with a small band at 574 cm^{-1}. The band at 1384 cm^{-1} is arising from B-O stretching vibrations of $(BO_3)^{3-}$ units. A band at 994 cm^{-1} is attributed to the B-O bond stretching of BO_4 units. The absorption band at 704 cm^{-1} indicates the B-O-B bending vibrations. The peak at 574 cm^{-1} could be due to loose BO_4 units. From Figure 2, it is evidenced that, there exists a distinctive difference in the relative intensities of the peaks due to B–O bonds of BO_3 and BO_4 functional units in BBLi and BBAl glasses. The ratio of the intensities of two bands $[I(BO_4)/I(BO_3)]$ was found to be varying with the type of modifier (Li or Al) ion present in the glass system. The values thus evaluated are found to be 0.81 and 0.95 for BBLi and BBAl glasses, respectively indicating that the relative fraction of BO_4 units could be more in the barium borate glass with Li^+ ions than with Al^{3+} ions. In general, the band at 806 cm^{-1} is assigned to the boroxol ring in the borate glass network. In the present study, a peak at 806 cm^{-1} is found to be missing, which indicates the absence of a boroxol ring in the glass network. The band at 2358 cm^{-1} is assigned to the stretching vibration of O-H and the band in the region of 3200-3600 cm^{-1} is ascribed to a hydroxyl group or water. The absorption band at 3445 cm^{-1} is attributed to a symmetric OH stretching mode.

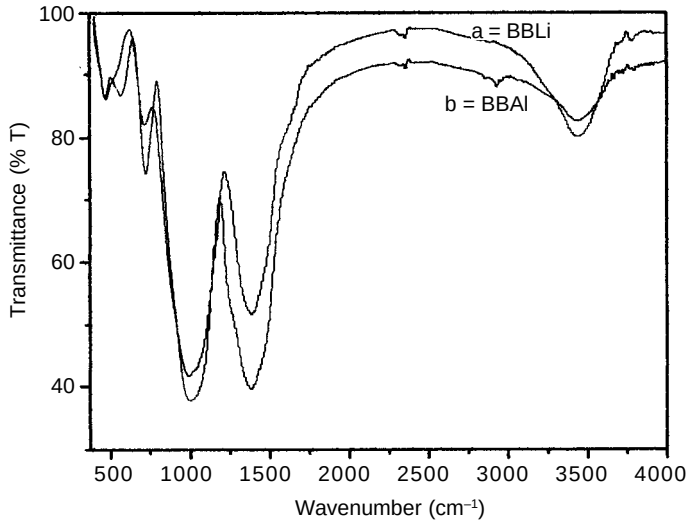

Figure 2. FTIR spectra of BBLi and BBAl reference host glasses.

The thermal behaviors of two host glasses are shown in Figure 3, respectively. The DTA curve of the BBLi glass shows an endothermic peak at 134.6°C and another at 440°C two and finally a broad exothermic peak at 742°C. The first endothermic peak is related to the loss of OH and the decomposition of hydroxide. The point of slope change of the endothermic peak at higher temperature (440°C) indicates the glass transition temperature (T_g) as makred in the Figure. The exothermic peak at 742°C is attributed to crystallization. Similarly for BBAl glass, T_g and crystallization (T_c) peaks are detected at

411°C and 716°C respectively. The TG curve shows only a small weight loss about 1% in the complete range of investigation *i.e.* from 30°C to 1000°C in both the glasses studied.

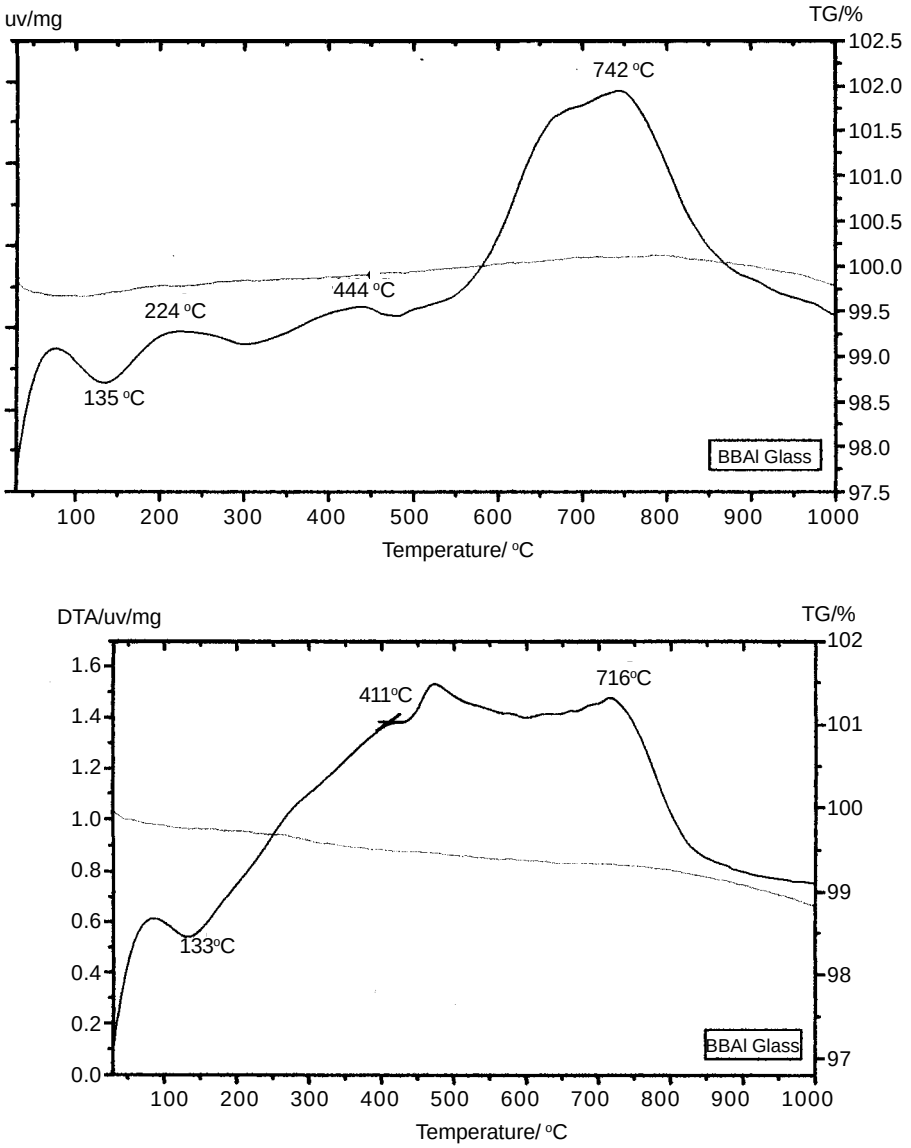

Figure 3. DTA & TG profiles of BBLi and BBAl reference host glasses.

Figure 4 presents both excitation and emission spectra of Eu^{3+} : BBLi/BBAl glasses. The excitation spectrum of the sample shows peaks corresponding to transitions from ground state to different excited states of 4*f*^{6} configuration of Eu^{3+} ions. The transitions are assigned appropriately to $^7F_0 \rightarrow {}^5F_2$ (304nm), $^7F_0 \rightarrow {}^5D_4$ (360nm), $^7F_0 \rightarrow {}^5G_2$ (381 nm), $^7F_0 \rightarrow {}^5L_6$ (392nm), $^7F_0 \rightarrow {}^5D_3$ (414nm), $^7F_0 \rightarrow {}^5D_2$ (463nm) and $^7F_0 \rightarrow {}^5D_1$

(531nm) respectively. Among all excitation bands, the $^7F_0 \rightarrow {}^5L_6$ (392nm) has been a prominent one and with which the emission spectrum has been obtained showing emission transition at 580nm ($^5D_0 \rightarrow {}^7F_0$), 593nm ($^5D_0 \rightarrow {}^7F_1$), 655nm ($^5D_0 \rightarrow {}^7F_3$) and 704nm ($^5D_0 \rightarrow {}^7F_4$). Among those five emission bands, the transition $^5D_0 \rightarrow {}^7F_2$ (615nm) has shown a strong *red* emission which is considered as a hypersensitive transition following the selection rules of $\Delta J = 2$. In glassy materials due to the absence of a centre of symmetry a mixing of the 4f orbitals with opposite parity could be taking place and hence an electric dipole transition (ED) would be found more intense [17-18] resulting in a bright *red* emission. The absence of emission from the excited levels of $^5D_{J=1,2,3}$ could be due to the presence of high energy phonons (~ 1380 cm^{-1}) from glasses. Under this condition, when the Eu^{3+} ions are excited to the $^5D_0$ level and above, there could be a fast non-radiative multiphonon relaxation taking place from those levels to the $^5D_0$ level from where the radiative transitions to the ground multiplet takes place. Therefore, $^5D_0 \rightarrow {}^7F_J$ emission transition intensities could be considered to represent the total emission intensity of the Eu^{3+} glass studied as was reported earlier in literature [19]. Figure 5 presents the decay curves as well as the lifetime of the prominent emission transition $^5D_0 \rightarrow {}^7F_2$ (615 nm) with an excitation wavelength 392 nm.

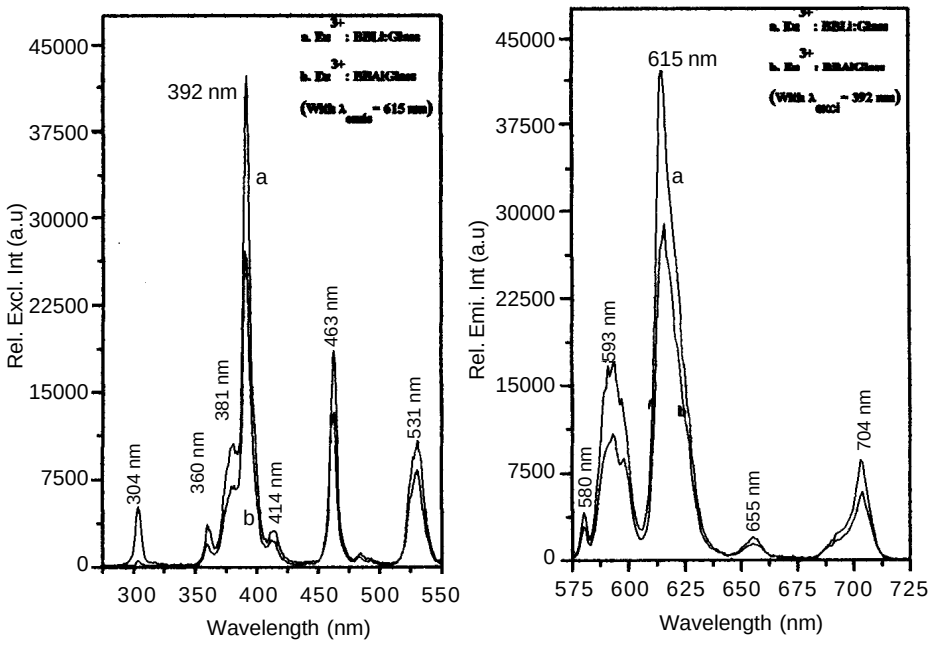

Figure 4. Excitation and emission spectra of Eu^{3+} : BBLi and BBAl glasses.

Figure 6 shows excitation and emission spectra of Tb^{3+} : BBLi/BBAl glasses. The excitation spectrum shows a sharp peak at 376 nm due to the transition $^7F_6 \rightarrow {}^5G_6$ along with a small component at 350 nm ($^7F_6 \rightarrow {}^5L_9$). The prominent excitation band at 376nm

has been chosen to measure the emission spectra of Tb^{3+} : BBLi/BBAl glasses and has revealed four emission peaks at 491nm, 547nm, 588nm and 624nm which are assigned to transitions $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$, respectively [20-21]. The

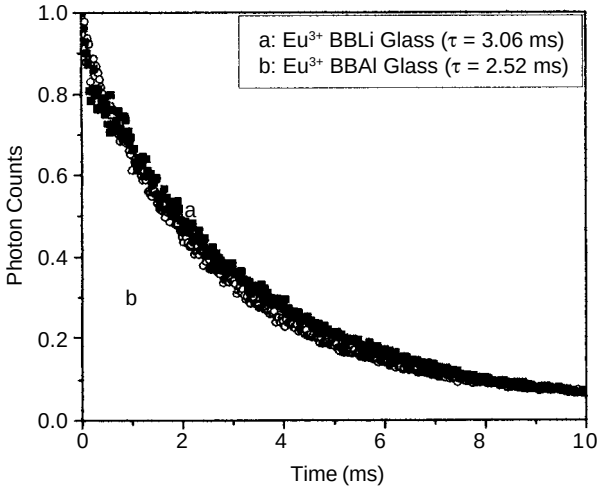

Figure 5. Decay curves of the red emission at 615nm of Eu^{3+} : BBLi and BBAl glasses (λ_{exci}= 392 nm).

emission transitions are all found to be intense and sharp due to the f-f inner shell transitions, from the excited level to the lower level such as $^5D_4 \rightarrow {}^7F_J$ (J = 3–6) for Tb^{3+} arises from the Laporte-forbidden transitions [22]. Here, green emission at 547nm ($^5D_4 \rightarrow {}^7F_6$) obeys the magnetic dipole transition selection rule of $\Delta J = \pm 1$ and is found to be

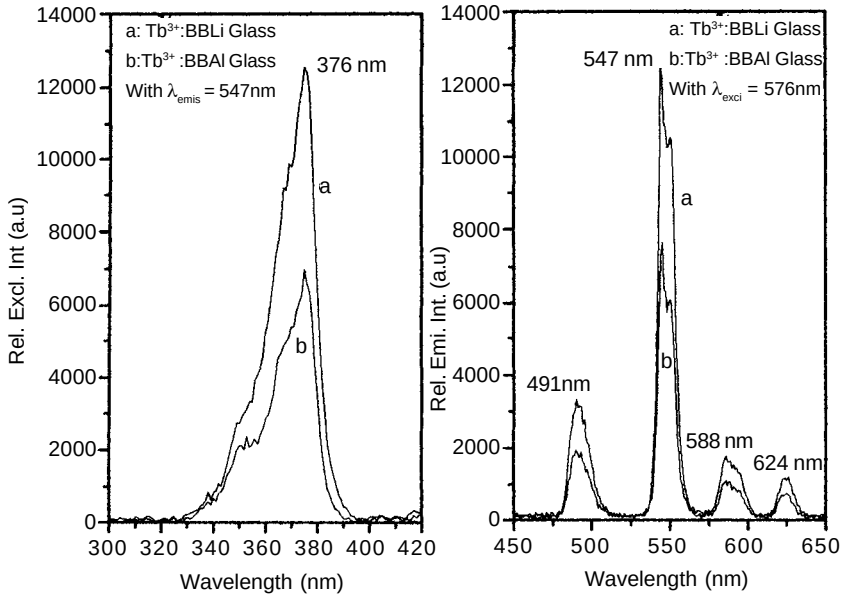

Figure 6. Excitation and emission spectra of Tb^{3+} : BBLi and BBAl glasses.

more intense. Figure 7 presents the decay curves of the green emission (547 nm) for both the glasses studied.

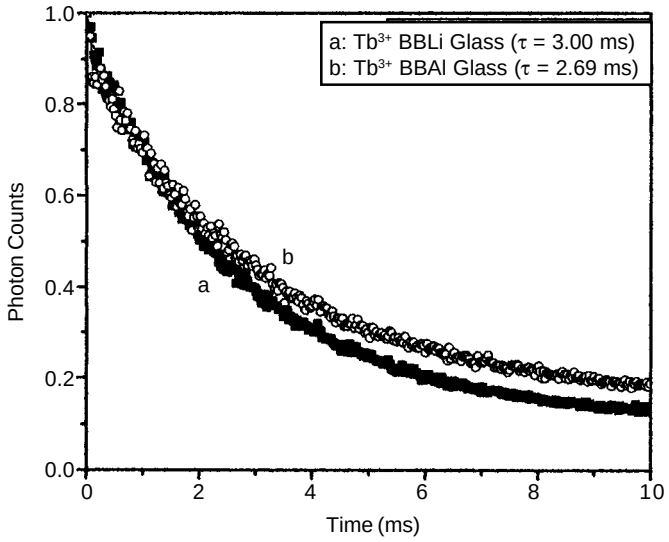

Figure 7. Decay curves of the green emission at 547nm of Tb^{3+} : BBLi and BBAl glasses (λ_{exci}= 376nm).

Figure 8a shows excitation and emission spectra of Ho^{3+} : BBLi/BBAl glasses. The excitation spectrum of Ho^{3+} glass reveals an excitation band at 389 nm ($^5I_8 \rightarrow {}^5G_4$). In the Figure 8b, a prominent green emission has been observed at 519nm ($^5F_4 \rightarrow {}^5I_8$) with 389nm.Two distinct local maxima are present which reflect the closely spaced

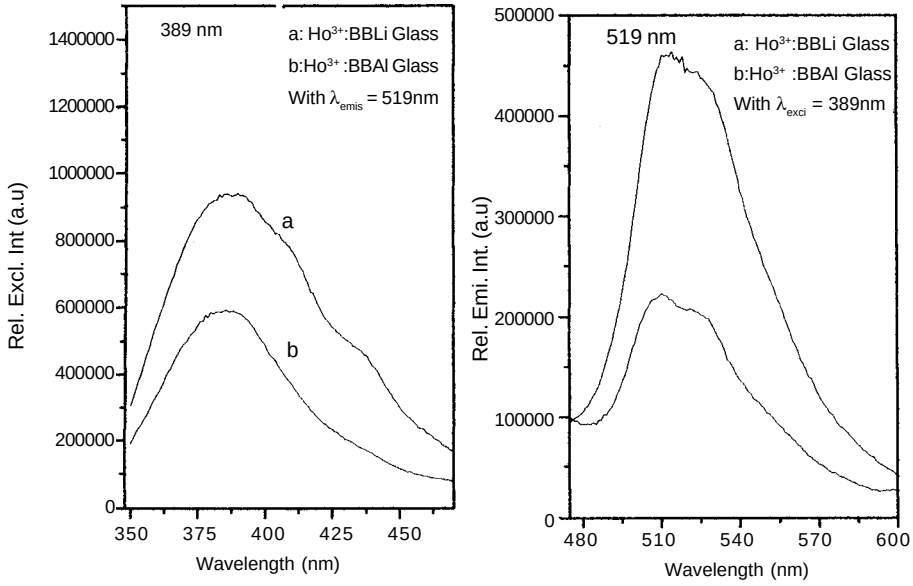

Figure 8. Excitation and emission spectra of Ho^{3+} : BBLi and BBAl glasses.

$^5F_3$ and $^5S_2$ stark manifolds of Ho^{3+} [23]. Figure 9 describes the decay curves of the emission transition $^5F_4 \rightarrow {}^5I_8$ along with the lifetime results. It is well known that the lifetime of an emission level is inversely proportional to the probability per unit time that

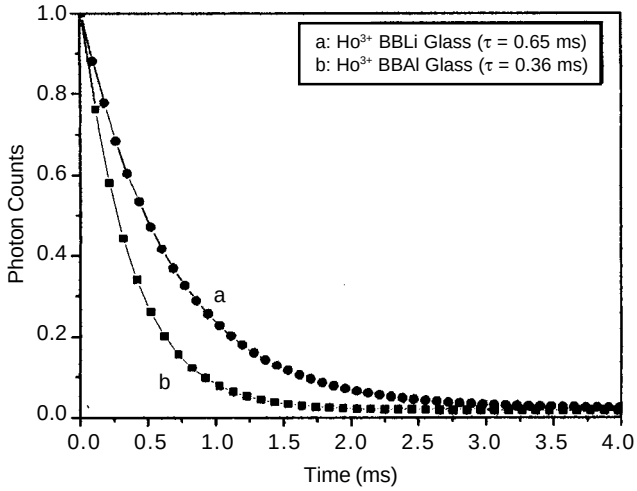

Figure 9. Decay curves of the *bluish green* emission at 519nm of Ho^{3+} : BBLi and BBAl glasses (λ_{exci}= 389nm).

the ion will exit from that excited level. In other words, the population of an excited level decays exponentially with a time constant equal to the lifetime [24-27]. When there are several pathways for the population to decay, the total probability is the sum of the individual probabilities for each pathway. The two main pathways for decay are radiative and nonradiative, and hence the lifetime is given by

$$\frac{1}{\tau_r} = \tau_r^{-1} + \tau_{nr}^{-1}$$

where τ is the total lifetime, is the radiative lifetime, and τ_{nr} is the non-radiative lifetime. The radiative lifetime arises from the fluorescence from an excited level to all the

Table 1. Measured lifetimes (τ_m in ms) and decay constants (k in $10^3 s^{-1}$) *or* inverse of the lifetimes (τ_m^{-1}) of the intense emissions of RE^{3+} (Eu^{3+}, Tb^{3+} & Ho^{3+}) : B_2O_3 – BaO – LiF/AlF_3 Glasses.

Emission parameters	Eu^{3+} doped B_2O_3–BaO–LiF/AlF Glasses *Red Emission* ($^5D_e \rightarrow {}^7F_2$) λ_{emiss} = 615 nm with $_{exci}$ = 392nm		Tb^{3+} doped B_2O_3–BaO–LiF/AlF Glasses *Green Emission* ($^5D_4 \rightarrow {}^7F_5$) $_{emiss}$ = 547nm with $_{exci}$ = 376nm		Ho^{3+} doped B_2O_3–BaO–LiF/AlF Glasses *Bluish Green Emission* ($^5D_4 \rightarrow {}^5F_8$) $_{emiss}$=519nm with $_{exci}$ = 389nm	
	LiF	AlF_3	LiF	AlF_3	LiF	AlF_3
T_m (m.sec)	3.06	2.52	3.00	2.69	0.65	0.36
$K = T_m^{-1} 10^3 s^{-1}$	0.326	0.396	0.333	0.371	1.538	2.777

levels below it. Non-radiative lifetime depends largely on the glass composition and the coupling between the vibrations of the lattice ions and the states of the rare earth ions. Decay curves are observed to be exponential and 1/e lifetimes have been computed. Table 1 gives the results concerning the measured lifetimes ( ), and also the inverse of the lifetimes (τ^{-1}) of the intense emissions of the rare earth glasses studied. Results clearly demonstrate the better performance with Li containing glasses with all three rare-earth ions as luminescent ions in the glasses. LiF has particularly been more effective as the glass network modifier in enhancing emission efficiency compared to AlF_3 containing glasses. It is due to the monovalent nature of Li^+ ions which are more mobile compased to the trivalent Al^{3+} ions in the glass matrices investigated. Another important reason is that Al^{3+} ions could function both as the network modifying and forming ions, therefore an effective influence is possible only from Li^+ in modifying luminescence properties of the rare earth ions in such optical glasses.

4. Conclusion

In summary, the barium fluoro-borate glasses containing two different modifiers (LiF, AlF_3) doped with Eu^{3+}, Tb^{3+} and Ho^{3+} ions have successfully been prepared and analyzed their measuring luminescence spectra. Also XRD, DTA and FTIR tools have been employed to understand their thermal and structural properties. An intense *red* emission from Eu^{3+} glassess, bright *green* emission from Tb^{3+} glasses and *bluish-green* emission from Ho^{3+} glasses have been noticed under an UV source and also from the measured emission profiles. Based on those results it could be suggested that Li containing glasses could be more promising and potential luminescent optical systems.

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